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Performance of an Infrared Photoacoustic Single Gas Analyzer in Measuring Ammonia from Poultry Houses

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TECHNICAL NOTE:

PERFORMANCE OF AN INFRARED PHOTOACOUSTIC SINGLE GAS ANALYZER IN MEASURING AMMONIA FROM POULTRY HOUSES

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ABSTRACT. *A single-gas photoacoustic analyzer, Chillgard RT, was evaluated for its performance of measuring ammonia (NH_3) concentrations in poultry production under laboratory and field conditions, using a multi-gas photoacoustic analyzer, INNOVA 1412, as a reference method. Calibration gases were used to evaluate the cross-interferences of carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), and water vapor on NH_3 measurements by Chillgard RT. The response times of Chillgard RT and INNOVA were measured in the laboratory using four vessels containing broiler litter. Side-by-side field comparisons between the Chillgard RT and INNOVA were conducted on a laying-hen farm and a broiler farm over two five-month periods. A strong linear relationship existed between the Chillgard RT and INNOVA NH_3 readings. The NH_3 measurement by the Chillgard RT showed no effect by CO_2, N_2O, CH_4, or water vapor under typical operational conditions in poultry operations. The Chillgard RT demonstrated a faster response to NH_3 than the INNOVA. Following 120-s measurements, the Chillgard RT and INNOVA achieved 99.6% and 96.7% of the expected values, respectively, when the INNOVA was configured at a 30-s sampling interval. The INNOVA response time was positively affected by water vapor level in the air samples. The Chillgard RT overestimated NH_3 concentrations by 3.24%, 10%, and 22.9% for laying-hen houses, stored boiler litter, and broiler houses, respectively, as compared to the INNOVA. Thus, performance of the Chillgard RT should be carefully validated before used in field NH_3 measurements.*

Keywords. *Ammonia, Analyzer, Gas Measurement, Photoacoustic, Poultry.*

High levels of ammonia (NH_3) in animal houses could adversely affect the health of animals and farm workers. Aerial NH_3 is considered a precursor in fine particulate matter (PM) formation; and its deposition can affect ecological nitrogen balance and cause eutrophication (Asman et al., 1998). Measurement of NH_3 concentration is essential for animal feeding operations (AFOs) management and emission determination and mitigation. Various types of analytical instruments based on different detection principles have been evaluated and used to measure NH_3 concentration in AFOs. Colorimetric detection tube (CDT) and passive samplers (PS) are inexpensive but only suitable for semi-quantitative, time-weighted-average measurements with limited sampling frequency and points. Electrochemical (EC) sensor and chemical-cassette (CC) tape based colorimetric analyzer provide economical solutions to continuous measurement due to their relatively low cost and long life span (Liang et al., 2004). Fourier transform infrared (FTIR) and chemiluminescence (CL) based analyzers offer best accuracy and sensitivity but are expensive and normally require a clean and controlled environment to operate. Other infrared-based technologies, such as photoacoustic spectrometer (PAS), near-infrared (NIR), open-path laser (OPL), have been widely used for both point and area source measurements.

Determining NH_3 emissions from AFOs requires continuous or semi-continuous measurements of NH_3 concentration with good sensitivity and wide dynamic measurable ranges. For area source and downwind fence line monitoring, the typical NH_3 concentration is lower than 1 ppm. FTIR, CL, PAS, and OPL techniques are appropriate due to their capability of detecting sub-ppb level NH_3. Harper et al. (2010) used OPL to measure downwind NH_3 concentrations, combined with measured micrometeorological data, and to quantify emissions from broiler houses in the San Joaquin Valley of California with backward Lagrangian stochastic (bLS) model. For monitoring emissions from point sources (e.g., animal house air exhaust) with relatively high NH_3 concentrations,

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PAS, CL, NIR, EC, and CC may be selected because of their wide detection range (0 to ~100 ppm or higher). It is challenging to find a sensor or analyzer that is suitable for poultry operations and can withstand harsh environmental conditions including high concentrations of corrosive gases (e.g., NH_3 and H_2S), particulates and microorganisms, as well as large variability in temperature and relative humidity. PAS based multi-gas analyzers have been widely used for laying hen, broiler, and turkey emission studies over the past decade and demonstrates excellent detection limit, accuracy, repeatability, and response time (van der Peet-Schwering et al., 1999; Xin et al., 2009; Li and Xin, 2010; Li et al., 2011; Li et al., 2012; Lin et al., 2012a,b). PAS has been recognized by U.S. Environmental Protection Agency (EPA) and used by the National Air Emission Measurement Study (NAEMS) project for NH_3 measurements in poultry, swine, and dairy operations (Ni and Heber, 2008). Our laboratory comparison study (unpublished data) had demonstrated the equivalency of the PSA multi-gas (including NH_3) analyzer used in the current paper to an EPA-approved CL analyzer for measuring NH_3 generated from poultry manure. Chillgard RT (Mine Safety Appliances Company, Pittsburgh, Pa.) is a single gas monitor and operates on the PAS principle, allowing a continuous measurement of NH_3 concentration. This instrument has been used in several agricultural NH_3 emissions studies in United States for its advantages over other NH_3 analyzers, including stability, low cost, and minimal maintenance (Li et al., 2008a). The main drawbacks and concerns about the validity and quality of data obtained with Chillgard RT include its high detection limit (1 ppm) and susceptibility to potential interference by moisture content and other gaseous constituents in the sample air from poultry operations.

The objective of this study was to evaluate the operating performance of a single-gas Chillgard RT with regard to measurement uncertainty, repeatability, stability, and interference of moisture when measuring aerial NH_3 from laying-hen and broiler facilities under laboratory and field conditions.

MATERIALS AND METHODS

PHOTOACOUSTIC GAS ANALYZER

Photoacoustic spectroscopy measures the effects of light absorption by solids, liquids, and gases by means of acoustic detection (Malkin and Cahen, 1979). For gas detection, it converts light absorbance (at wavelengths characteristic of an analyte) to acoustic signals, and in general delivers better sensitivity than conventional infrared (IR) gas spectrometry. Figure 1 illustrates the schematic of a photoacoustic gas analyzer. The IR light from a tungsten lamp is first modulated by a mechanical chopper and then passed through a narrow-band optical filter to remove all wavelengths except for the "measuring wavelength" characteristic of a target gas. In the measurement chamber, the target gas molecules become energized upon light absorption, and dissipate the absorbed energy in the form of heat. The chopper-modulated pulsed

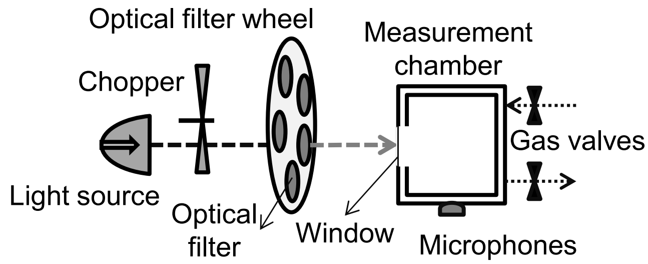

Figure 1. Schematic of a photoacoustic gas analyzer's operation.

light results in periodic heat expansion and contraction of the sample air, creating sound. The acoustic signal is recorded by microphones and converted to an electrical signal correlated to gas concentration.

The single-gas Chillgard RT analyzer was originally designed for monitoring NH_3 concentrations typical of 1 to 1000 ppm with a sensitivity of 1 ppm and an accuracy of ±2 ppm in refrigeration systems (Chillgard RT Manual, 2013). An internal vacuum pump draws air samples in at a flow rate varying from 0.75 to 1 LPM, depending on the size (e.g., length and diameter) of air sampling tubing and inlet. Its display reading updates every 7 s and can be recorded on a computer via analog input (0 to 10 VDC) or RS-232 serial connection.

An INNOVA 1412 multi-gas analyzer (LumaSense Technologies, Inc., Santa Clara, Calif.) served as a reference method and was compared with Chillgard RT under different laboratory and field conditions. Two INNOVA analyzers were equipped with five optical filters for measuring NH_3, carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), and water vapor, respectively. The sampling pump of the INNOVA drew air samples of up to 1.8 LPM to the measurement chamber where the samples were analyzed for different gases by different optical filters. The display readings of the INNOVA updated every 30 s and were stored in the internal memory. The data were exported to a computer via RS-232 or RS-485 connection. The instrument had an NH_3 detection limit of 0.44 ppm with 1-s sampling and integration time (INNOVA gas detection limits, 2011).

The Chillgard RT and INNOVA analyzers were challenged weekly and calibrated, as needed, with zero, 23 (for laying hens), or 53 ppm (for broilers) NH_3 (All zero or span gases were balanced with ultra-high-purity N_2 unless otherwise noted), 3000 ppm CO_2, 5.02 ppm N_2O, and 105 ppm CH_4 gas calibration standards (Certified plus or EPA grade, Matheson Tri-gas, Swedesboro, N.J.). The concentrations of the calibration standards were selected based on the actual gaseous concentrations in poultry operations and the availability of the standards.

LABORATORY EVALUATION WITH STANDARD GASES

A laboratory evaluation system was built to assess the Chillgard RT for interference of CH_4, CO_2, N_2O, and water vapor on NH_3 measurement (fig. 2). Mass flow controllers (GFC-17S, Aalborg, Orangeburg, N.Y.) were used to dilute gas calibration standards (53 ppm NH_3, 3000 ppm CO_2, 5.02 ppm N_2O, and 100 ppm CH_4) to various challenge concentrations (table 1). A total of 12 concentration

Table 1. Combinations of different gas concentrations for laboratory evaluation of Chillgard RT.

ID	NH_3 (ppm)	CO_2 (ppm)	N_2O (ppm)	CH_4 (ppm)	Dew point (°C)	Chillgard (ppm)[a]	INNOVA (ppm)[a] NH_3	INNOVA CO_2	INNOVA N_2O	INNOVA CH_4
1	53	0	0	0	-	53 (0)	52.8 (0.19)	4.61 (4.75)	0.03 (0.01)	0.63 (0.21)
2	0	3000	0	0	-	0 (0)	0.401 (0.22)	3035 (10.5)	0.07 (0.02)	1.84 (0.36)
3	0	0	5.02	0	-	0 (0)	0.264 (0.07)	8.96 (7.99)	5.04 (0.01)	1.19 (0.45)
4	0	0	0	100	-	0 (0)	0.342 (0.07)	8.04 (4.68)	0.03 (0.02)	101.6 (0.33)
5	0	0	0	0	19.8	0 (0)	0.206 (0.15)	8.28 (5.93)	0.03 (0.02)	0.71 (0.61)
6	26.5	1500	0	0	-	27 (0)	26.6 (0.15)	1518 (7.5)	0.06 (0.03)	2.26 (0.65)
7	26.5	0	2.5	0	-	27 (0)	26.4 (0.19)	7.33 (5.24)	2.50 (0.01)	0.92 (0.73)
8	26.5	0	0	50	-	27 (0)	26.8 (0.14)	4.79 (6.58)	0.02 (0.02)	50.38 (0.68)
9	26.5	0	0	0	13.5	27 (0)	26.5 (0.09)	0.05 (2.54)	0.05 (0.03)	-0.14 (3.31)
10	18	1000	0	0	11.1	18 (0)	17.7 (0.15)	1013 (4.0)	0.08 (0.04)	3.03 (1.49)
11	18	0	1.7	0	11.1	18 (0)	17.4 (0.27)	-4.33 (4.54)	1.71 (0.01)	-1.74 (2.03)
12	18	0	0	34	11.1	18 (0)	17.6 (0.14)	1.15 (6.98)	0.25 (0.03)	35.7 (0.55)

[a] Chillgard and INNOVA concentrations: mean (standard deviation).

combinations were tested, at an environmental temperature of 20°C and a total gas flow rate of 3 LPM. Calibration gases were diluted and mixed in a polytetrafluoroethylene (PTFE) manifold (mixing manifold) before proceeding to a second manifold (sampling manifold) where gases were sampled for analysis. Each concentration combination was tested for 5 min and the NH_3 readings of both Chillgard RT and INNOVA at the end of the 5-min period were compared. PTFE tubing's (4 mm o.d. × 3 mm i.d. for INNOVA and 6.35 mm o.d. × 3.18 mm i.d. for Chillgard RT) were used and the tubing length between the sampling manifold and each analyzer was 1 m.

Laboratory Evaluation System: Using Broiler Litter

One Chillgard RT and one INNOVA were selected to monitor NH_3 gas concentrations from four 19-L plastic vessels containing broiler litter (fig. 3). Both air inlet and outlet were located on the air-tight lid of the vessel. Samples of the exhaust air from each vessel were sequentially taken using an air sampling pump (Model BTC-IIS, Parker Hannifin, Hollis, N.H.) at 5-min intervals. This sampling sequence yielded a measurement cycle of 25 min for the entire system (including 5 min for the ambient air). The successive sampling was accomplished through controlled operation of four solenoid valves (Model 456654, Burkert, Irvine, Calif.). An inline Teflon-membrane filter (4.7 cm dia., 5 µm pore dia.) was mounted upstream of each solenoid valve. The vessels were operated under negative pressure and were placed in an environment-controlled 20°C room. Analog outputs from the Chillgard RT and digital outputs from the INNOVA were logged on a computer at 1-s intervals using a data acquisition (DAQ) module (Model USB-2416, Measurement Computing Corporation, Norton, Mass.) and a LabVIEW (National Instrument Corp., Austion, Tex.) program. The program also averaged all the raw measurement data over 60-s intervals and recorded them in a data file. Fluorinated ethylene propylene (FEP; 6.35 mm o.d. × 3.97 mm i.d.) tubing was used except for the tubing (PTFE) between the sampling manifold and gas analyzers.

Field Evaluation: Laying Hens

One Chillgard RT and One INNOVA were installed in a mobile air emissions monitoring unit (MAEMU) on site to continuously collect data on NH_3, CO_2, CH_4, and N_2O concentrations and emissions from three laying-hen houses on a commercial farm in Iowa. The three identical laying-hen houses had high-rise style, with manure storage in the lower level and no supplemental heating. Air samples were drawn from two composite sampling points in the manure storage of each house, as well as from an air inlet located on the ceiling of one of the houses to provide the ambient background data. Each sampling point was equipped with dust filters to keep large particulates from plugging or contaminating sample line, servo valves and delicate gas analyzers. A positive-pressure gas sampling system (PP-GSS) was used in the MAEMU and continuously pumped air samples from each sampling point using a dedicated air pump (fig. 4). The sample air was bypassed when not analyzed. Air samples from each location were collected sequentially over 2-min period via the controlled operation

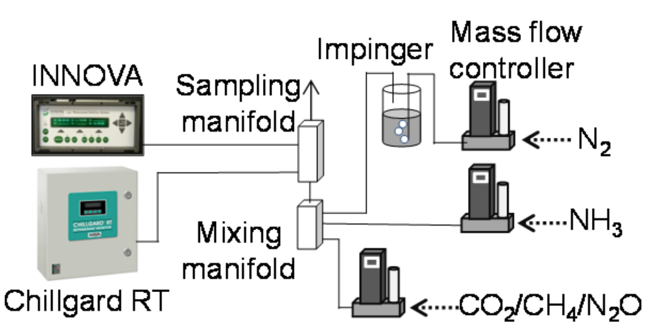

Figure 2. Schematic of laboratory system setup for gaseous interference evaluation.

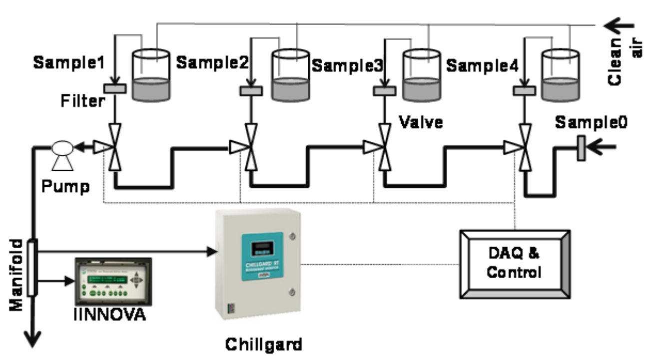

Figure 3. Schematic of the laboratory system setup for the Chillgard RT evaluation. The system measured NH_3 concentrations of air samples from four broiler litter vessels.

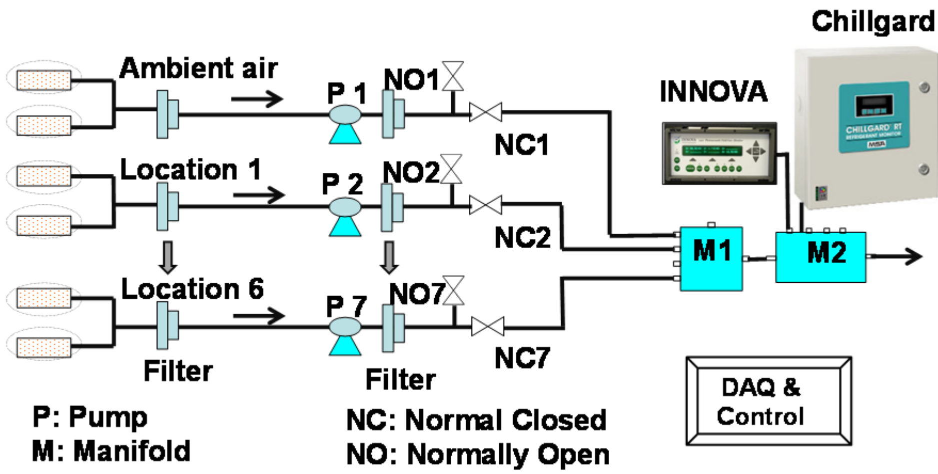

Figure 4. Schematic of the field system setup on a laying-hen farm for the Chillgard RT evaluation. The system measured NH_3 concentration at six composite sampling points and an air inlet in three high-rise laying-hen houses.

of the servo valves of the PP-GSS. Every 2 hours, air samples from the ambient (background) location were drawn and analyzed for 8 min. FEP (9.53 mm o.d. × 6.35 mm i.d.) tubing was used except for the tubing (PTFE) between the sampling manifold and gas analyzers.

Field Evaluation: Broilers

Two identical broiler houses on a commercial farm in Delaware were monitored for air emissions with the INNOVA and Chillgard RT. Built-up litter was used and only top-caked litter was removed after each 42-day grow-out during this monitoring study. Liquid propane radiant heaters were used during brooding periods and cold seasons when housing temperature dropped below setting temperatures. Air sampling equipment, gas analyzers, and data acquisition and control system were housed in a temperature-controlled cabinet in one of the houses' control room. Air samples were drawn from two sampling points in each broiler house. A negative-pressure gas sampling system (NP-GSS) was used and it collected air samples from each sampling point using two pumps, one for gas analyzers and the other for bypass air (fig. 5). Air samples from each location were collected sequentially over 3-min period via the controlled operation of the servo valves of the NP-GSS. FEP (6.35 mm o.d. × 3.97 mm i.d.) tubing was used except for the tubing (PTFE) between the sampling manifold and each analyzer.

A compact Fieldpoint device (CFP-2020, National Instrument Corp., Austion, Tex.) programmed with LabVIEW was used for data acquisition and system control in both laying hen and broiler field evaluations. Temperatures in animal houses, MAEMU, and equipment cabinets were monitored, along with the dew point of air samples. Heating tapes and thermostats were used to heat the air sampling tubing to >30°C, preventing potential moisture condensation. The analog outputs of the Chillgard RT and INNOVA were recorded at 1-s intervals and then averaged over 60-s intervals.

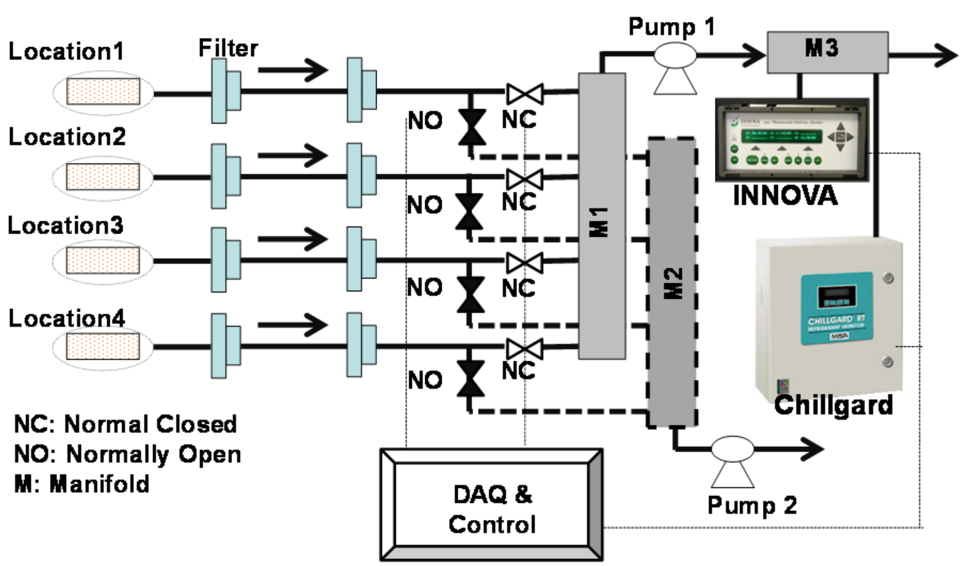

Figure 5. Schematic of the field system setup on a broiler farm for the Chillgard RT evaluation. The system measured NH_3 concentration at four air sampling points in two broiler houses.

Data Analysis

Analog outputs of the Chillgard RT were converted to NH_3 concentrations to match the display readings. Statistical analyses of the Chillgard RT and INNOVA measurement results were performed with analysis of variance (ANOVA) using standard least squares of JMP (SAS Institute, Cary, N.C.). Significant differences for all comparisons were based on $P<0.05$.

Results and Discussion

Cross-Interference of CH_4, CO_2, N_2O, and Water Vapor

The cross-interferences of CH_4, CO_2, N_2O, and water vapor on NH_3 measurement are well recognized by the INNOVA manufacturer. An algorithm, embedded in the instrument's internal memory, automatically corrects NH_3 readings based on the concentrations of other gaseous constituents. Comparatively, no such correction is available to the Chillard RT; and it is stated in the manual that Chillgard RT is cross-sensitive to CH_4. However, our experiments showed that, within the test concentration ranges (NH_3: 0 to 50 ppm; CO_2: 0 to 3000 ppm; N_2O: 0 to 5 ppm, CH_4: 0 to 100 ppm), none of the four gases had a significant cross-interference on NH_3 measurement ($P>0.14$). The drift of NH_3 readings caused by CH_4 was estimated to be 1 ppm NH_3 per 5,000 ppm CH_4. In poultry houses, CH_4 concentrations are well below this level. Thus, no cross-interference of CH_4 was noted given the resolution of NH_3 measurement (1 ppm) by the Chillgard RT.

Response Times of Chillgard RT and INNOVA

Air samples from broiler-litter vessels and ambient air were sequentially measured for 5 min each and the last reading during the 5-min analysis was used as the final stabilized reading. The 30-s instantaneous readings by the Chillgard RT and INNOVA over a 45-min period are plotted to illustrate the time for them to respond to step changes in concentration (response time) (fig. 6a). The dynamic concentrations at 30-s intervals were compared to the final stabilized reading and the percentage responses were calculated and presented in figure 6b. For all tested NH_3 concentrations, Chillgard RT showed a quicker response than INNOVA. It took 120 s for the Chillgard RT to reach a >95% expected value when samples were switched from ambient air to NH_3-laden airs; whereas it the INNOVA 180 s. Flushing both instruments with NH_3-laden air prior to the measurement, the average 95% response time (T95) of the Chillgard and INNOVA decreased to 90 and 120 s, respectively. Water vapour could affect the response time of the INNOVA as its T95 decreased with the increasing dew-point temperature of air samples ($P<0.01$). Upon a sudden change in NH_3 concentration, the Chillgard RT and INNOVA reached an average of 99.6% and 96.7% full responses, respectively, after 120 s (fig. 7). The INNOVA's response time can be shortened by reducing the numbers of optical filters used. For instance, for single-gas measurement, the sampling interval of INNOVA (between two readings) could be set to 20 s and the response of INNOVA at 120 s would increase to 98.6%.

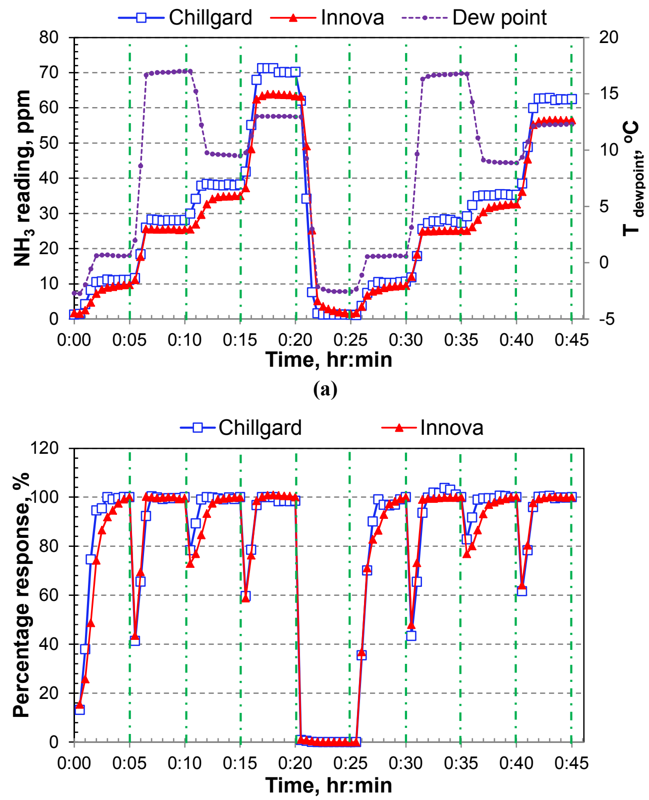

Figure 6. Response times of the Chillgard RT and INNOVA for air samples with different ammonia concentrations (a: dynamic ammonia concentration; b: percentage of dynamic concentration to stabilized concentration during each 5-min sampling). Vertical dash lines indicate changes in air samples.

Chillgard RT vs. INNOVA with Broiler Litter

The Chillgard RT measured higher NH_3 concentrations than the INNOVA when monitoring NH_3 gas emissions from broiler litter (fig 6a). To further examine such differences, we compared the NH_3 readings of the Chillgard RT and INNOVA at multiple response times,

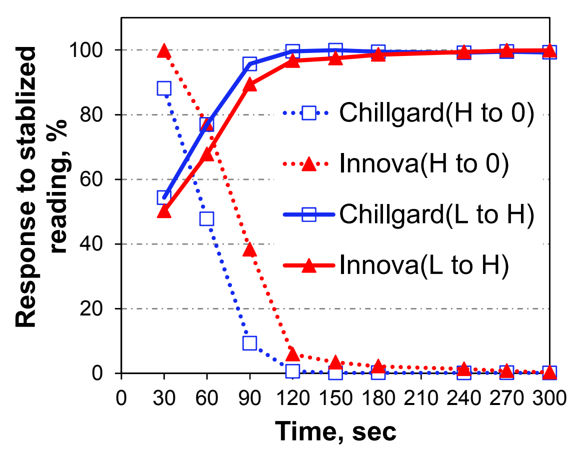

Figure 7. Average response times of the Chillgard RT and INNOVA. (H to 0: concentration change from high to zero; L to H: concentration change from low to high).

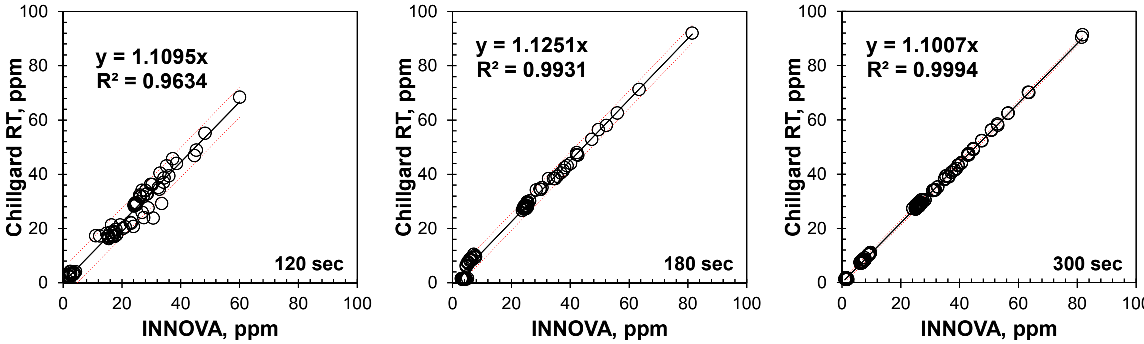

Figure 8. Relationship of ammonia readings with the Chillgard RT *vs.* INNOVA at 120, 180, and 300 s. The dashed lines below and above the regression lines represent 95% confidence intervals of the observations.

including 120, 180, and 300 s (fig. 8). All paired comparisons yielded an excellent linearity ($R^2 > 0.96$). The NH_3 readings given by the Chillgard RT were 11.0%, 12.5%, and 10.0% higher than those derived from the INNOVA at 120-, 180-, and 300-s response time, respectively. The P-values of the paired t-tests were all <0.0001, indicating significant differences. The difference may have resulted from the co-existence of other gas constituents (e.g., hydrocarbons) with NH_3 in the air sample, which might share similar light-adsorption wavelengths to NH_3. Trabue et al. (2010) reported the top 25 speciated non-methane hydrocarbons (NMHCs) and their concentration levels in a commercial broiler house. The NMHC species and concentrations differed with and without birds inside the house. Their concentrations were related to litter conditions and ventilation rate, and showed a similar time-series trend to NH_3 concentration (Burns et al., 2007; Li et al., 2008b). The cross-sensitivity of the Chillgard RT and INNOVA to most NMHC compounds was specified in the manual by the manufacturer except for *o*-xylene, propane, and pentane. On the other hand, the interference of NHMCs on NH_3 measurement (i.e., NH_3 detection selectivity) is affected by the band (e.g., width of transmitting wavelengths) of the optical filter used. Different filters employed by the Chillgard RT and INNOVA, thus, would result in their different susceptibility to the interference by NHMCs and accordingly different NH_3 readings.

Chillgard RT vs. INNOVA in Laying-Hen and Broiler Houses

Figure 9a compares NH_3 concentrations measured by the Chillgard RT and INNOVA in the high-rise laying-hen manure storage, with readings acquired at the end of every 2-min sampling period. Laying hen NH_3 concentrations derived from the Chillgard RT were 3.2% higher than those from the INNOVA; however, in the broiler houses, the Chillgard RT readings were 22.9% higher (fig. 11b). The gas composition of the exhaust air from laying-hen and broiler houses could be significantly different. For example, liquid propane is typically burned for supplemental heating in broiler houses during winter while no supplemental heating is provided in laying-hen houses. The compositions of laying-hen and broiler feces can be different due to different feed formulation and nutrient content, which may result in different volatile organic compounds (in both composition and concentrations) when the feces is degraded by microorganisms. The results of this study suggest that the Chillgard RT should be evaluated by a reference method, such as chemiluminescence, FTIR, or INNOVA for cross-interferences from uncharacterized volatile organic compounds. The Chillgard RT may be good for mitigation studies that focus on relative changes in NH_3 concentration. But for emission monitoring (e.g., emission inventory development), the measurement bias by the Chillgard RT should be fully checked and be properly corrected prior to use.

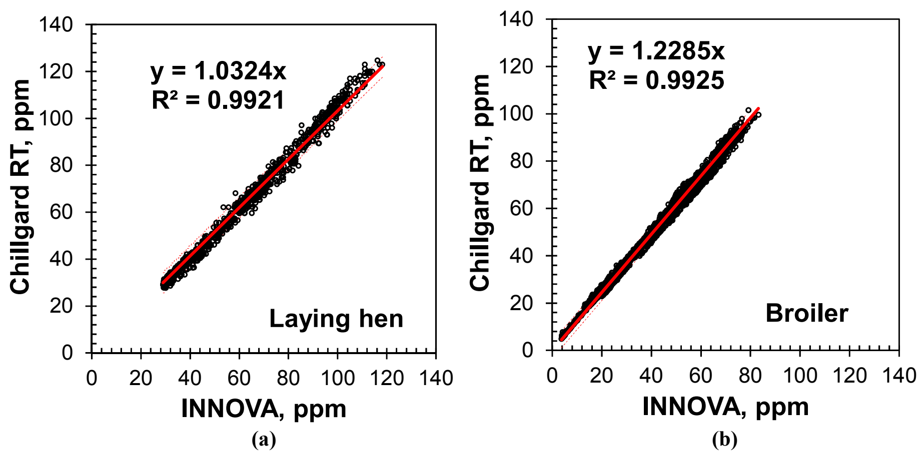

Figure 9. Comparison of ammonia readings measured by the Chillgard RT vs. INNOVA during two field monitoring events (a: laying hens with 1395 points; b: broilers with 2602 points).

CONCLUSIONS

A commercially available single photoacoustic analyzer, Chillgard RT, was evaluated and compared with a multi-gas photoacoustic analyzer, INNOVA 1412, for real-time continuous monitoring of NH_3 in poultry operations. The following conclusions can be drawn:

1. The NH_3 readings by the Chillgard RT were not significantly affected by CO_2, N_2O, CH_4, or water vapor under typical operational conditions in poultry houses.
2. The Chillgard RT has a quicker response than the INNOVA. The Chillgard RT and INNOVA achieved an average of 99.6% and 96.7% expected values, respectively, after 120 s measurement when the INNOVA was configured at a 30-s sampling interval.
3. There was a strong linear relationship between Chillgard RT and INNOVA under all the experimental conditions. The Chillgard RT overestimated NH_3 concentrations by an average of 3.24%, 10%, and 22.9% for measurements with the laying-hen houses, stored boiler litter, and broiler houses, respectively.
4. Performance of the Chillgard RT should be evaluated using certain reference NH_3 analyzers, such as chemiluminescence, FTIR, and INNOVA before used for monitoring concentrations and emissions in a new environment.

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